



Synthesis, Characterization, and Oxidation of Copper (I) Complexes Using N,N,N-Pincer Ligands

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Abstract

D-block metals show great promise in inorganic catalytic research. Particularly, copper, a d-9 metal, has contributed to the catalytic properties of pincer complexes. Copper pincer complexes were obtained through attachment of copper (I) metal to tridentate di-pyrazole-3,6-di-tert-butyl-carbazole, a N,N,N-pincer ligand. This ligand changes the metal geometry, affecting its reactivity. We used lithium di-isopropyl amide to deprotonate the ligand and reacted it with copper (I) chloride to obtain complexes **1** and **2**. Upon acquiring nuclear magnetic resonance spectra and X-ray crystal structures, oxidation studies were performed to give structures **3**, **4** and **5**. Using complexes 1-5, electron transfer self-exchange rate studies were performed to provide insight into the differences in electron transfer rates between the methyl and isopropyl complexes

Background

In recent chemical research, inorganic copper systems have been intensively studied to understand how the copper ion dictates rapid electron transfer with enzymes, particularly relating to the electron transport chain. A novel Cu₂N₂ diamond core structure supported by a bis(2-tert-butylsulfanylphenyl)amido) ligand has displayed “a fully reversible one-electron redox process between a reduced Cu(I)-Cu(I) complex and a Cu(1.5)-Cu(1.5) state”.² With this diamond core structure, the studied copper complex shows potential to enhance rapid electron transfer, similar to that of cytochrome *c* oxidase which completes electron transfer among a Cu_A site. While these complexes only show two oxidation states, we aim to produce a copper complex with an additional oxidation state.

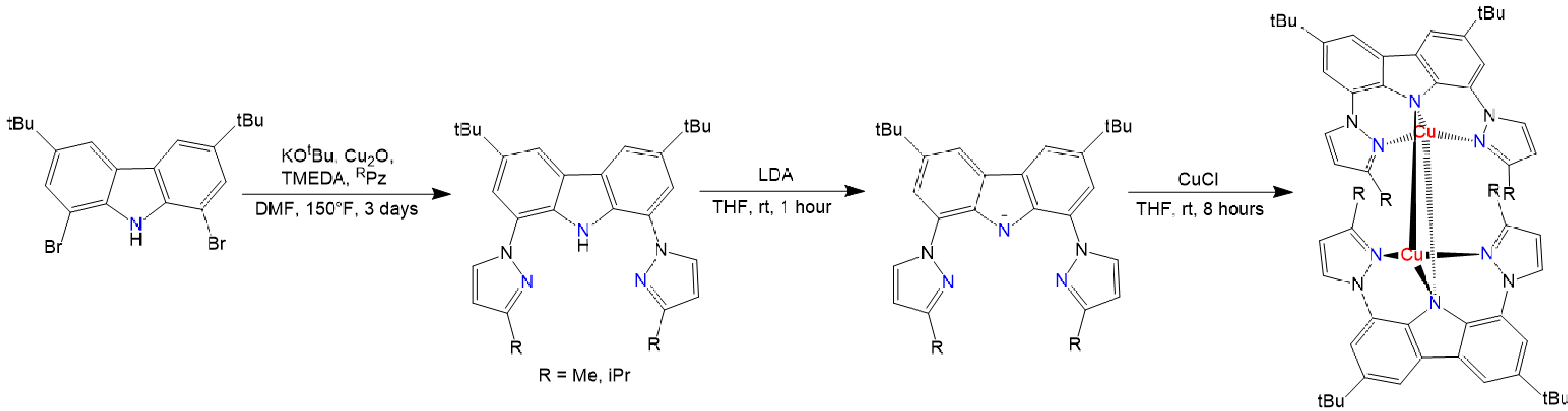
Conclusion

Two copper (I) complexes supported by a N,N,N-pincer ligand were synthesized and characterized using Nuclear Magnetic Resonance Spectroscopy, X-ray crystallography, Cyclic Voltammetry and UV-Vis Spectroscopy. The synthesis reactions yield dimeric products, with two copper metal centers supported by two ligands. Molecular structures reveal that the metal centers exist out of the plane of the ligand, making it more accessible for redox reactions. Oxidation of the complexes with FcPF₆ and AgPF₆ suggest that the copper complexes can exist in Cu(I)-Cu(I), Cu(1.5)-Cu(1.5), and Cu(II)-Cu(II) oxidation states. While the electron transfer self-exchange rate studies were only preliminary, they give a suggestion that the methyl complexes have faster electron transfer rates.

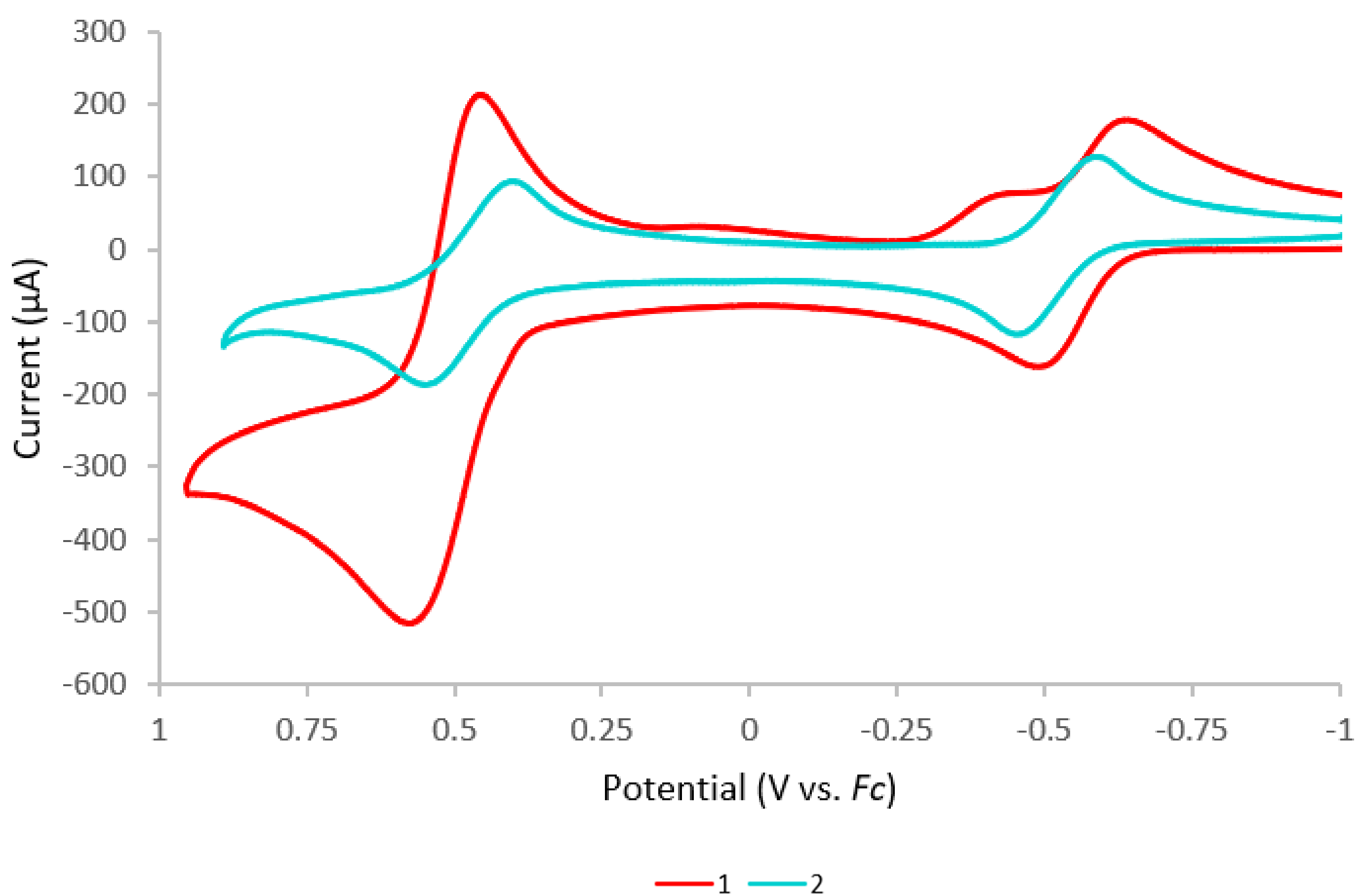
Acknowledgements

This research is supported by Loyola University Chicago and the Mulcahy Research Fellowship Program.

Synthesis

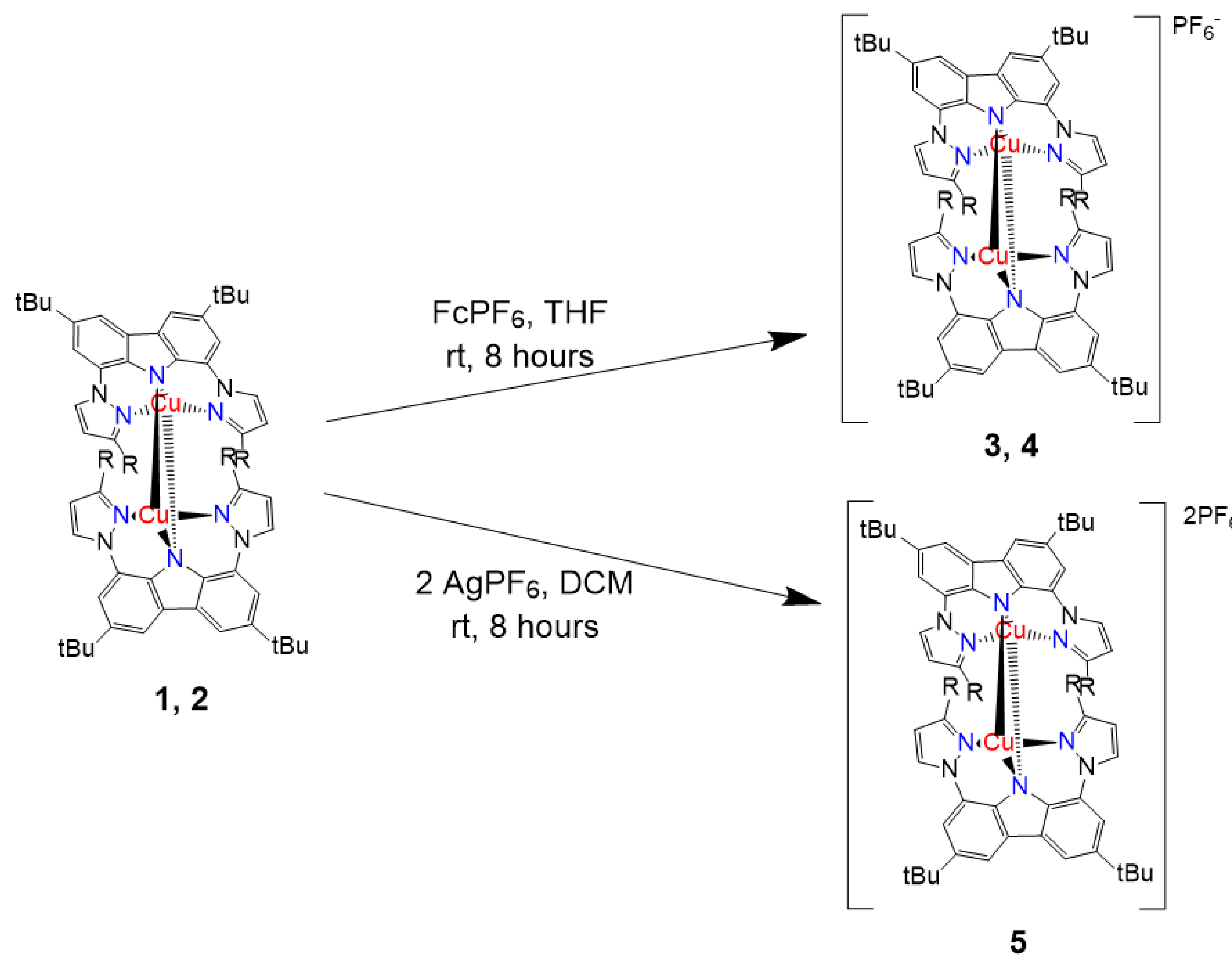


Cyclic Voltammetry



NBu₄PF₆⁻, Solvent: THF; Working electrode: glassy carbon; Scan rate: 0.1 V/s.

Oxidation



Electron Transfer Self-Exchange Rate

Equation to calculate electron transfer rate (k_{ex}):

$$k_{ex} = 4\pi X_d X_p (\Delta\nu / (W_{dp} - X_p W_p - X_d W_d)) C_{tot}$$

- X_d and X_p are the mole fractions of the diamagnetic and paramagnetic species
- $\Delta\nu$ is the chemical shift difference between the pure diamagnetic and paramagnetic species in Hz
- W_{dp} is the peak width at ½ height signal of interest
- W_d and W_p are the peak widths of pure diamagnetic or paramagnetic species
- C_{tot} is the total concentration of the exchanging species in M

Results from Methyl Complexes (1 & 3)

Fraction of 1	Fraction of 3	k_{ex}
0.5	0.5	1.2×10^5

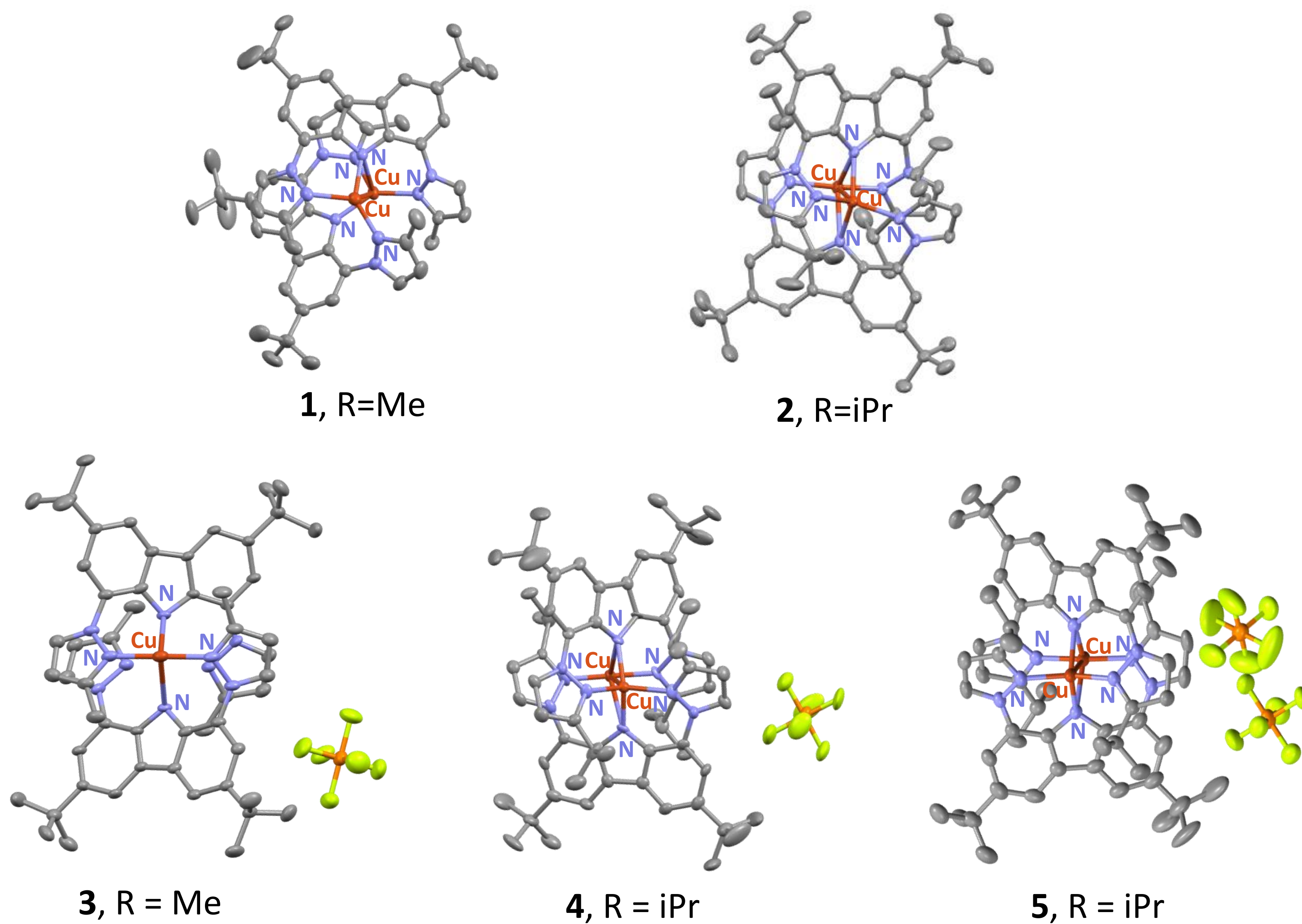
Results from Isopropyl Complexes (2 & 4)

Fraction of 2	Fraction of 4	k_{ex}
0.5	0.5	9.7×10^3

Results from Isopropyl Complexes (4 & 5)

Fraction of 4	Fraction of 5	k_{ex}
0.5	0.5	8.9×10^3
0.67	0.33	4.5×10^3

Molecular Structures



1) Harkins, Seth B.; Peters, Jonas C. Amido-Bridged Cu₂N₂ Diamond Cores that Minimize Structural Reorganization and Facilitate Reversible Redox Behavior between a Cu₂Cu₁ and a Class III Delocalized Cu_{1.5}Cu_{1.5} Species. *J. Am. Chem. Soc.* [Online] **2004**, 126, 2885-2893

2) Jameson, Donald L.; Anand, Rajan. Examination of Electron Transfer Self-Exchange Rates Using NMR Line-Broadening Techniques: An Advanced Physical Inorganic Laboratory Experiment. *J. Am. Chem. Ed.* [Online] **2000**, 77 (1), 88-89